

INTENSITY-DISTRIBUTION IN MOLECULAR-SPECTRA : CLASS I SYSTEMS OF HgCl AND HgBr

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Plate III

ABSTRACT. Using the slit-width method and a calibrated quartz Kipp and Zonen standard ribbon lamp, the "peak intensities" have been determined for the bands of the Class I system of HgCl³⁵ and HgBr³¹ lying in the region between $\lambda 2650$ and $\lambda 2400$. The transition probabilities for the various bands in each system have hence been derived. These experimental values have been found to agree with Condon's theoretical considerations. The Morse energy function was assumed for drawing the potential energy curves. The effective temperature of the source has been estimated assuming Maxwell-Boltzmann distribution.

INTRODUCTION

The intensity distribution in bands extending over long spectral regions is but little investigated and only in the case of a few molecules have quantitative data been obtained. Ornstein (1928), Elliot (1930), Johnson and Tawde (1932), and Tawde (1934) among others made accurate measurement of the intensities of certain band systems due to lighter molecules. Mercury chloride and mercury bromide are comparatively heavier molecules, giving rise to prominent band systems in the ultra-violet in the region between $\lambda 2700$ - 2400 and quantitative estimate of the intensities of these are considered to be of value in relation to the Franck-Condon theory (Jevons). The present paper gives the results of such determination with respect to the Class I systems of these two molecules HgCl and HgBr.

EXPERIMENTAL

The intensity technique and the photographic procedure adopted in the present case are essentially the same as those used by Johnson and Tawde (1932). For work in the ultra-violet region in which the bands were situated, a quartz standardised ribbon lamp calibrated by a monochromator down to $\lambda 2400$ and supplied by Kipp and Zonen was used. The bands were obtained in a discharge tube as described in the previous papers by the author (Sastry, 1941). Photographs were taken with a Hilger medium quartz spectrograph and Ilford special rapid plates were used throughout. With the usual precautions in adjusting the times of exposure and in developing the plates the grain effect is found negligible. Plates with varying times of exposure were used to calculate the intensities of the weaker as well as the stronger band heads. The calibration

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proper wave-lengths. A photograph of one such set of typical curves taken on a plate of HgCl is shown in Plate III, Fig. 3. The values of the optical density $\log(u/u_0)$ for the different steps are calculated for a particular wave-length, say λ , at which the band head is situated. In finding the true density of the band head at any point the density of the background of the photographic plate at that point is subtracted from that of the band head at the same point. Plotting the density values of the intensity marks against $\log I$ (where $I = I_{\lambda} d\lambda \times w$) the density curve was obtained. From this curve the intensity corre-

TABLE II

 I/v^4 and I values HgBr^{A1}

Weight	v''	0	1	2	3	4	5	6	7	8	9
2720.0	0	1000.0 450.4	1420.0 652.8	1075.0 503.7	792.7 378.4	601.3 336.4	452.9 224.6	343.7 173.7			
2621.4	1	1535.0 676.1	738.9 331.3	—	671.4 312.9	839.9 399.0	762.6 369.1	651.2 321.0	422.4 212.0	—	—
2576.3	2	1058.0 455.0	769.5 337.7	945.0 422.1	527.3 240.0	266.5 123.2	075.8 177.5	652.2 313.9	515.8 302.1	410.5 205.0	—
2000.5	3	730.7 306.8	917.7 392.9	458.7 200.4	566.5 252.2	486.2 220.3	235.1 108.2	—	660.2 320.6	408.8 199.1	—
1629.9	4	449.4 184.8	1670.0 609.3	486.7 207.8	599.2 260.6	—	615.5 277.4	—	—	—	—
887.8	5	—	651.2 266.8	760.3 320.4	296.7 126.1	—	—	—	156.0 71.0	222.4 103.5	—
706.0	6	—	275.7 110.5	794.0 324.4	—	—	—	271.7 119.2	—	—	—
580.0	7	—	—	432.4 172.6	640.9 260.6	358.8 151.9	347.7 146.8	—	—	—	—
344.4	8	—	—	—	447.1 178.0	—	—	—	—	—	—
217.6	9	—	—	—	26.0 19.1	410.5 166.4	126.7 50.9	—	—	—	—
141.5	10	—	—	—	—	304.9 156.6	203.8 104.2	—	—	—	—
125.1	11	—	—	—	—	95.9 37.3	225.0 87.1	96.6 38.0	—	—	—
151.7	12	—	—	—	—	—	188.7 71.6	207.6 80.1	—	—	—
160.5	13	—	—	—	—	—	—	199.0 75.3	221.4 85.2	—	—
140.1	14	—	—	—	—	—	—	—	204.8 77.3	163.6 62.8	—
53.5	15	—	—	—	—	—	—	—	—	53.15 19.96	86.9 33.3

TABLE III
Transition Probabilities, HgCl

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8	9	10	11
0	.29	.42	.11	.06	.04	.04						
1	.33	.	.17	.18	.12	.09	.06	.05				
2	.12	.19	.10	.09	.12	.14	.09	.08	.07			
3	.04	.20	.10	.16	.06	.08	.11	.08	.09	.08		
4	.02	.06	.24	.09	.15	.11	.09	.09	.	.	.13	
5	.02	.05	.26	.24	.13	.14	.16					
6	.	.05	.09	.33	.20	.22	.09					
7	.	.00	.06	.22	.41	.	.31					
8			.01	.09	.28	.25	.	.37				
9				.03	.29	.37	.32					
10					.05	.48	.36	.19				
11						.10	.59	.31				
12							.13	.36	.29			
13								.42	.47	.32		
14											.10	

TABLE IV
Transition Probabilities, HgBr

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8	9	10	11	12
0	.17	.26	.19	.14	.12	.08	.06						
1	.26	.13	.	.12	.15	.14	.12	.08					
2	.18	.13	.16	.09	.05	.07	.12	.12	.08				
3	.15	.20	.10	.13	.11	.05	.	.16	.10				
4	.11	.43	.13	.16	.	.09							
5		.30	.36	.1408	.12				
6		.16	.46	.	.22	.	.17						
7			.30	.45	.	.25							
8			.	.52	.28								
9				.05	.37	.23							
10					.26	.74							
11						.70	.30						
12						.47	.53						
13							.47	.53					
14								.55	.45				
15									.37	.44			

sponding to the density of the band head at λ was read off. On account of the rapidly varying sensitivity of the plate it was found necessary to plot a separate density curve for each wave-length at which a band head was situated and as many curves were drawn as there were band heads whose intensities had to be determined.

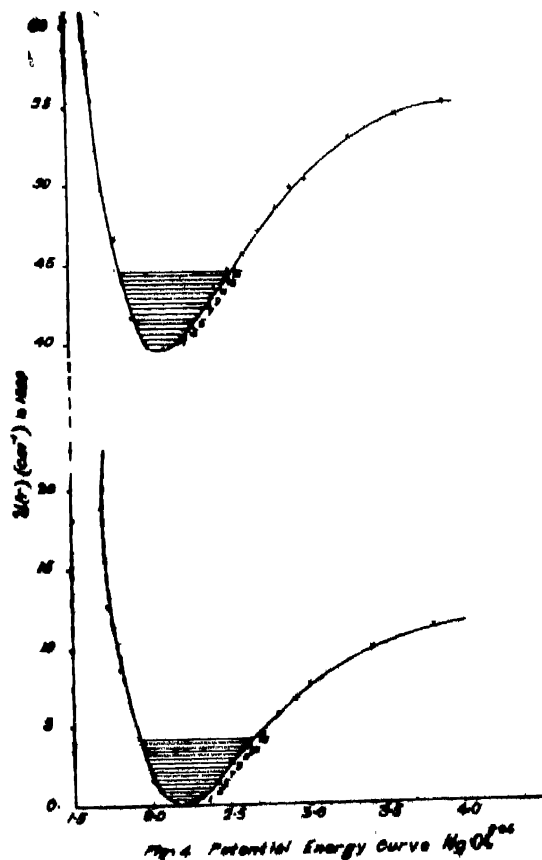
The final values of the intensities thus obtained for all the band heads of the Class I systems of HgCl are shown in Table I on the scale of 1000 for the (0,0) band. Table II gives similar values in the case of HgBr.

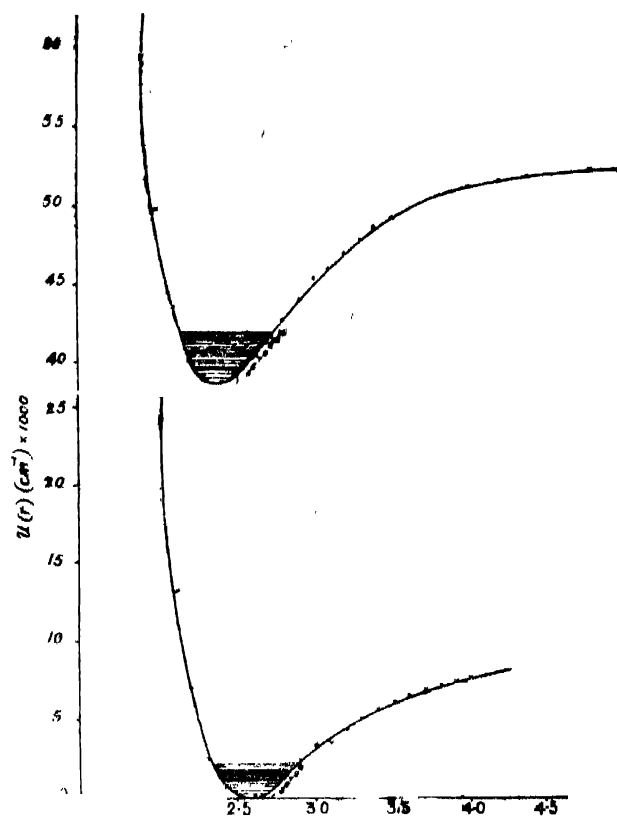
Immediately below the numbers denoting the intensities in the above tables are given the I/ν^4 values of the bands, ν being calculated from the vibration constants given at the end.

The $\sum \frac{I}{\nu^4}$ values corresponding to the initial state ν' are given in the same tables under column "Weight." The quotient of the I/ν^4 values of any band and the "Weight" of the initial state represents the transition probability. These probabilities are given in Tables III and IV for HgCl and HgBr.

THEORETICAL

The potential energy curves (Figs. 4 and 5) drawn to scale for the upper and



Fig. 5. Potential Energy Curve HgBr^{81}

lower states involved in the emission of the Class I systems of HgCl^{35} and HgBr^{81} are drawn with the aid of the Morse function

$$U(r) = D_e \left[1 - e^{-a(r-r_e)} \right]^2$$

in which the constants (Sastry, 1941) are found to be for HgBr

$$D'_e = 13740 \quad a' = 1.81 \quad r'_e = 2.36$$

$$D''_e = 8863 \quad a'' = 1.83 \quad r''_e = 2.53$$

and for HgCl

$$D'_e = 17040 \quad a' = 1.75 \quad r'_e = 2.06$$

$$D''_e = 12660 \quad a'' = 1.74 \quad r''_e = 2.17$$

The vibrational constants employed in the above calculation are given below (Wieland, 1927).

	HgCl^{35}	HgBr^{81}
ν_e	39700.5	38754.4
ω'_e	341.4	228.5
x''_e, ω'_e	1.71	.95
ω''_e	292.5	186.5
x''_e, ω''_e	1.69	.975

From these curves, the parabola representing the maximum probability of transition was derived by the graphical method suggested by Condon (Jevons, p. 70). This parabola is superposed in its correct position on the data given in Tables III and IV for HgCl and HgBr. In the case of HgCl the parabola is narrower than HgBr and the distribution agrees well with the experimental values.

In HgBr the parabola is slightly out of step with the experimental values. This might be due to the superposition of the unresolved isotopic band heads, which in the case of bromine are of equal intensity the abundance ratio of the Br⁷⁹ and Br⁸¹ being 1 : 1. More probably it is due to the inadequacy of the Morse function.

A peculiar feature that is noticed in the theoretical derivation of the parabola in both band systems is that one arm is developed more than the other: this feature is in very good agreement with experiment which shows distinctly that the sequences of bands in both HgCl and HgBr towards the violet end are better developed than towards the red.

E F F E C T I V E T E M P E R A T U R E S

The first column in Tables I and II gives the number of molecules in the various initial vibrational states. Assuming that this is a distribution in thermal equilibrium at temperature T of the source, we have, according to Maxwell-Boltzmann,

$$N = N_0 e^{-E_v/kT}$$

$$\text{so that} \quad hc \left[\omega'_v \left(v' + \frac{1}{2} \right) - x'_v \omega'_v \left(v' + \frac{1}{2} \right)^2 \right] = kT \cdot \log_e \frac{N_0}{N'_{v+\frac{1}{2}}}$$

Substituting the various constants for HgCl²¹ system

$$3411.1 \left(v' + \frac{1}{2} \right) - 1.71 \left(v' + \frac{1}{2} \right)^2 = 1.6083 T \log_e \frac{N_0}{N'_{v+\frac{1}{2}}}$$

The numbers N_0 and $N'_{v+\frac{1}{2}}$ are given by the 'Weights' corresponding to the respective initial vibrational levels. Plotting the vibrational energy against the ratio $\log_e \frac{N_0}{N'_{v+\frac{1}{2}}}$ the absolute temperatures are obtained directly. The effective temperatures thus derived in the case of HgCl is about 1500°K and for HgBr 1800°K.

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